PROCESSES FOR OXIDATIVE DEHYROGENATION

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BACKGROUND OF THE INVENTION

This application is related to co-pending U.S. Patent Application No. 09/___,___ (Attorney Docket No. 98-25) to Liu, filed on February 22, 1999 and incorporated herein by reference.

Field of the Invention

10   This invention relates to methods and materials for the dehydrogenation of alkanes, particularly the conversion of ethane to ethylene, and more particularly, to mixed oxide catalysts for oxidative dehydrogenation of ethane.

Discussion

Ethylene can be produced by thermal cracking of hydrocarbons, and by nonoxidative

15   dehydrogenation or oxidative dehydrogenation of ethane (ODHE). The latter process is attractive for many reasons. For example, compared to thermal cracking, high ethane conversion can be achieved at relatively low temperatures (about 400 °C or below). Unlike thermal cracking, catalytic ODHE is exothermic, requiring no additional heat to sustain reaction. Furthermore, in contrast to catalytic dehydrogenation, catalyst deactivation by coke formation

20   should be minimal in ODHE because of the presence of oxygen in the reactor feed. Other alkanes can similarly be oxidatively dehydrogenated.

In the late seventies, Thorsteinson and coworkers first disclosed useful low temperature ODHE catalysts comprised of mixed oxides containing molybdenum, vanadium, and a third transition metal. E. M Thorsteinson et al., "The Oxidative Dehydrogenation of Ethane over

25   Catalyst Containing Mixed oxide of Molybdenum and Vanadium," 52 J. Catalysis 116-32 (1978). Later studies examined families of alumina-supported vanadium-containing oxide

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catalysts, MV and MVSb, where M is Ni, Co, Bi, and Sn. R. Juarez Lopez et al., "Oxidative Dehydrogenation of Ethane on Supported Vanadium-Containing Oxides," 124 <u>Applied Catalysis A: General</u> 281-96 (1995). More recently, Schuurman and coworkers describe unsupported iron, cobalt and nickel oxide catalysts that are active in ODHE. Y. Schuurman et al., "Low

5   Temperature Oxidative Dehydrogenation of Ethane over Catalysts Based on Group VIII Metals," 163 <u>Applied Catalysis A: General</u> 227-35 (1997). Although the mixed oxide catalysts reported by Thorsteinson, Schuurman and others might be useful discoveries, they represent a small fraction of potentially active inorganic oxide mixtures.

Industrial interest has stimulated investigations into new catalysts and methods for

10   improved performance (e.g., conversion and selectivity) for the oxidative dehydrogenation of alkanes. There is a need for new dehydrogenation catalysts and methods.

SUMMARY OF THE INVENTION

This invention discloses catalysts and methods for the oxidative dehydrogenation of alkanes that have from 2 to 4 carbon atoms and particularly ethane to ethylene. These catalysts primarily include nickel oxide and catalyze oxidative dehydrogenation with conversions of greater than 5% and with selectivity of greater than 70%. An object of the present invention is to provide a process whereby a C_2-C_4 alkane can be oxidatively dehydrogenated to one or more olefins with relatively high levels of conversion and selectivity. A further object of this

20   invention is to provide a catalyst that selectively catalyzes the reaction of a C_2-C_4 alkane with oxygen to produce one or more corresponding C_2-C_4 olefins with relatively high levels of conversion and selectivity, meaning preferably without the concurrent production of significant amounts of by-products, such as carbon monoxide or carbon dioxide.

In general, the catalysts of this invention have as a required component nickel oxide and

25   it is an object of this invention to provide a catalyst for the oxidative dehydrogenation of an alkane into one or more olefins having nickel oxide (NiO). The nickel oxide is combined with other metal oxides, dopants, carriers, binders and/or fillers into a catalyst that is contacted with a gas mixture. The gas mixture comprises at least the alkane and oxygen, but may also include diluents (such as argon, nitrogen, etc.) or other components (such as water or carbon dioxide).

Optionally, the gas mixture that contacts the catalyst may also include one or more of the olefin

products for an oxidative dehydrogenation process that converts a gas mixture having one ratio

of alkane to alkene to a gas mixture having a different ratio of alkane to alkene. The catalysts of

this invention include a material or composition of matter having the empirical formula:

5 $$Ni_xA_jB_kC_lO_i \qquad\qquad I$$

wherein Ni is nickel and x is in the range of about 0.1-0.96;

A is selected from the group consisting of Nb, Ta, Co and combinations thereof and j is

in the range of from about 0-0.8;

B is an element selected from the group consisting of alkali metals, alkaline earths, or

10 lanthanides and combinations thereof, including Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Mn, La, Ce,

Pr, Nd, Sm and combinations thereof and k is in the range of from 0-0.5;

C is an element selected from the group consisting of Sn, Al, Fe, Si, B, Sb, Tl, In, Ge, Cr,

Pb and combinations thereof and l is in the range of from 0-0.5;

i is a number that satisfies the valence requirements of the other elements present; and

15 the sum of j, k and l is at least 0.04.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows ethane conversion and ethylene selectivity as a function of reaction

temperature for Ni-Nb oxide mixtures and for an optimized Mo-V-Nb catalyst.

Fig. 2 shows ethane conversion and ethylene selectivity as a function of oxygen content

20 of reactor feed for Ni-Nb oxide mixtures and for an optimized Mo-V-Nb catalyst.

Fig. 3 shows ethane conversion and ethylene selectivity as a function of oxygen content

of reactor feed for Ni-Co-Nb oxide mixtures and for an optimized Mo-V-Nb catalyst.

DETAILED DESCRIPTION

25 The present invention includes nickel oxide catalysts for oxidative dehydrogenation of

alkanes having 2, 3 or 4 carbon atoms to the corresponding olefin(s). The invention is

exemplified for ethane to ethylene. An important feature of this invention is the relatively high

percentages of conversion and selectivity that the catalyst provides for a dehydrogenation

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process. As used herein the phrase selectivity (also known as efficiency) refers to a percentage that reflects the amount of desired olefin product produced as compared to the total carbon products as follows:

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$$\% \text{ selectivity } = 100 \text{ x } \frac{\text{Moles of alkene produced}}{\text{The molar alkene-equivalent sum (carbon basis) of all carbon-containing products, excluding the alkane in the effluent.}}$$

10 Similarly as used herein the term conversion refers to a percentage that reflects the amount of alkane provided to the reaction as compared to the total carbon products as follows:

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$$\% \text{ conversion } = 100 \text{ x } \frac{\text{The molar alkane-equivalent sum (carbon basis) of all carbon-containing products, excluding the alkane in the effluent.}}{\text{Moles of alkane in the reaction mixture, which is fed to the catalyst in the reactor}}$$

These expressions are the theoretical expressions for selectivity and conversion. Simplified
20 formulas have been used in the examples herein, and may be used by those of skill in the art. The simplified formula for % selectivity is % selectivity = 100 x [(moles of alkene)/(moles of alkene + ((moles of carbon dioxide)/2))]. Similarly the simplified formula for % conversion is % conversion = 100 x [(moles of alkene + ((moles of carbon dioxide)/2))/(moles of alkane)]. Although these simplified formulas are used, typically the only products observed in the ethane
25 to ethylene oxidative dehydrogenation reaction (using an ethane and oxygen gas feed) are ethylene and carbon dioxide. In these formulas, those of skill in the art will recognize that an alkene is an olefin. These calculations are straightforward when ethane and propane are the alkanes. When butane is the alkane, the possibility exists that the product is one or more of 1-butene, 2-butenes or 1,3-butadiene. Thus, the percentages for selectivity and conversion are
30 percentages of one or more of these dehydrogenated products of butane. Using the catalysts and

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process that are disclosed herein, selectivity of dehydrogenation of alkane to the corresponding

olefin can be greater than 70%, 75%, 80%, 85% and most preferably greater than 90%. Also, the

conversion can be greater than 5% and preferably greater than 10% or greater than 15%. In fact,

the conversions may be 20% or greater. Surprisingly, the experimental results suggest that the

5   selectivity does not alter significantly with the conversion, meaning that within experimental

error the selectivity is more or less independent of the conversion.

The catalysts of this invention include a composition of matter or material having the

empirical formula:

$$Ni_xA_jB_kC_lO_i \hspace{4cm} I$$

10   wherein Ni is nickel and x is in the range of about 0.1-0.96;

A is selected from the group consisting of Nb, Ta, Co and combinations thereof and j is

in the range of from about 0-0.8;

B is an element selected from the group consisting of alkali metals, alkaline earths, or

lanthanides and combinations thereof, including Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Mn, La, Ce,

15   Pr, Nd, Sm and combinations thereof and k is in the range of from 0-0.5;

C is an element selected from the group consisting of Sn, Al, Fe, Si, B, Sb, Tl, In, Ge, Cr,

Pb and combinations thereof and l is in the range of from 0-0.5

i is a number that satisfies the valence requirements of the other elements present; and

the sum of j, k and l is at least 0.04.

20   Catalysts defined by this formula include nickel that is substantially in the oxidized state;

meaning that there may be nickel metal present, but it will not be the majority. Nickel oxide

(NiO) is present in an amount preferably of at least 20% by weight, more preferably at least 50%

by weight and most preferable at least 60% by weight. In some preferred embodiments, Nb and

Ta are included together in the composition (with Co being optional) and j may range from about

25   0.05-0.8. Generally, x may range from about 0.1-0.96 (e.g., 10-96%), preferably from about 0.3

to about 0.85, more preferably from about 0.5 to about 0.8 and most preferably from about 0.6 to

about 0.8. Generally, j may range from about 0 to about 0.8 (e.g., 0-80%), but preferably ranges

from 0.04 to about 0.5, more preferably from about 0.04 to 0.4 and alternatively from about 0.3

to about 0.4. Generally, k and l each may range from about 0 to about 0.5 (e.g., 0-50%), but

30   preferably ranges from 0 to about 0.4, more preferably from about 0 to 0.1 and most preferably

from about 0 to about 0.05. Within these ranges, the sum of j, k and l will be at least about 0.04 but may range as high as about 0.9. In other embodiments, the sum of j, k and l will be no more than 0.5, 0.4 and optionally 0.3. In some embodiments, Nb and Ta are included together in the composition (with Co being optional) and j may range from about 0.04 to about 0.8 or in any of

5   the other listed ranges for j.

In still other embodiments, the catalysts can be represented by the empirical formula:

$$Ni_aCo_bNb_cTa_dSn_eK_fAl_gFe_hO_i. \qquad\qquad II$$

In formula II, subscripts b, c and d are numbers greater than or equal to zero but less than one. At least one of b, c and d is nonzero. Subscripts e and f are numbers greater than or equal to zero

10   but less than or equal to about 0.35; subscripts g and h are numbers greater than or equal to zero but less than or equal to about 0.10; and subscript a is a number greater than zero but less than one, and satisfies the expression:

$$a \le 1 - b - c - d - e - f - g - h. \qquad\qquad III$$

In equation II, subscript i is a number that satisfies valence requirements of elements listed in the

15   formula.

The catalyst is supplied to the reactor as a fixed bed—the catalyst may or may not be supported on a carrier. If a carrier is used, the carrier may be selected from the group consisting of alumina, silica, titania, zirconia, magnesia, zeolites, clays or mixtures thereof. The catalyst may take any form, including powder, split, granular, pellets or a shaped catalyst, such as tablets,

20   rings, cylinders, stars, ripped bodies, extrudates, etc. known to those of skill in the art. For example, the shaping of the mixture of starting composition may be carried out by compaction (for example tableting or extrusion) with or without a prior kneading step, if necessary with addition of conventional auxiliaries, for example graphite or stearic acid or its salts as lubricants. In the case of unsupported catalysts, the compaction gives the desired catalyst geometry directly.

25   Hollow cylinders may have an external diameter and length of from 2 to 10 mm and a wall thickness of from 1 to 3 mm. Very generally, the mixture of starting composition metal may be shaped either before or after the calcination. This can also be carried out, for example, by

comminuting the mixture after the calcination and applying it to inert supports to produce coated

catalysts. However, the application can also be carried out before the final calcination. The

catalyst may be diluted (e.g., have its density reduced) with binders and/or inert fillers, which are

known to those of skill in the art, including for example quartz chips, sand or cement. Diluents

5   may be added to the catalyst in the range of from about 0 to about 30% by volume, preferably in

the range of from about 10 to about 25 % by volume. Preferred diluents improve the heat

removal or heat transfer of the catalyst to help avoid hot spots or to modify hot spots. Binders

generally provide mechanical strength to the catalyst and may be added in the range of from

about 0-30% by volume, preferably in the range of from about 5 to about 25 % by volume.

10   Useful binders include silica sol, silica, alumina, diamateous earth, hydrated zirconia, silica

aluminas, alumina phosphates, naturally occurring materials and cement and combinations

thereof. See, e.g., the discussion of supports, shapes, binders and fillers in U.S. Patents

5,376,613, 5,780,700 and 4,250,346, each of which is incorporated herein by reference for all

purposes. The percentages or amounts of binders, fillers or organics referred to herein relate to

15   the starting ingredients prior to calcination. Thus, the above is not intended to imply statements

on the actual bonding ratios, to which the invention is not restricted; for example during

calcination other phases can form.

The disclosed mixed oxides can be used to make an olefin from the respective alkane, for

example, ethylene from ethane, by contacting them, in a pressure vessel or reactor, with a gas

20   mixture comprised of the alkane and oxygen. Contact between the catalyst and the gas mixture

occurs by passing the gas mixture through the interstices in the fixed bed, which ensures intimate

contact between the gas mixture and the catalyst. Also, the gas mixture may be passed over the

catalyst surface, in situations were gas cannot pass through the catalyst. During contact, the

catalyst and the gas mixture are maintained at a temperature between about 250°C and 400°C.,

25   thus the reaction temperature is typically 400°C or less, preferably 325°C or less and

alternatively 300°C or less. The reaction pressure during contacting can range from about 0.5 to

20 bar and for a time of between 100 milliseconds to about 10 seconds. Generally, the gas

mixture that contacts the catalyst comprises the alkane to be dehydrogenated and oxygen or an

oxygen source in the reactor. The gas mixture may also include diluents such as nitrogen, argon

or carbon dioxide. In other embodiments, the gas mixture may also include water (e.g., steam) or butylenes or ethylene or propylene.

The disclosed catalyst can convert alkane to olefin (e.g., ethane to ethylene) even in the presence of significant amounts of olefin (e.g., ethylene) in the reactor feed. Typically the gas

5 mixture that is contacted with the catalyst has an oxygen content in the range of from about 0.01 to about 50% by volume and the alkane in the range of from about 5-99.99% by volume. A preferred range includes 0.01 to 20 % by volume of oxygen and 10 to 90 % by volume of alkane (e.g., ethane, propane or butane). In an alternative embodiment, the gas mixture can further include the olefin of the corresponding alkane that is being dehydrogenated. For example, an

10 ethane gas feed may also contain ethylene, such that the catalyst and methods of this invention will convert such a gas stream to a more olefin rich content. For example, a 70%/30% by volume ethane/ethylene reactant gas can be converted to a 60%/40% by volume ethane/ethylene product or a 50%/50% by volume ethane/ethylene product. Generally, mixed gas reactant streams may have an alkane/olefin range from about 99%/1% by volume to about 50%/50% by

15 volume. In another alternative, the gas mixture that contacts the catalyst may contain raffinate II, which is a mixture of butane, 2-butenes and 1-butene. Because of the ability of these catalysts to perform the desired dehydrogenation selectively, mixed streams may be converted into more uniform streams.

Generally, the catalyst can be prepared by sol-gel, freeze drying, spray drying,

20 precipitation, impregnation, incipient wetness, spray impregnation, ion exchange, wet mix/evaporation, dry mix/compacting, high coating, fluid bed coating, bead coating, spin coating, physical vapor deposition (sputtering, electron beam evaporation, laser ablation) and chemical vapor deposition. Thus, any technical or non-technical technique may be used. Also the catalyst may take any of the forms discussed above (granular, tablets, etc.).

25 One method for making the catalysts of this invention is by mixing solutions or suspensions that include the metal precursors, driving off the solvent and converting at least part of the precursors into oxides. See also U.S. Patent 4,250,346, incorporated herein by reference. The metal precursors comprise the desired metal in a solution or suspension in a desired amount in a suitable solvent. The metal precursor solution is prepared by dissolving a least part of a

30 soluble compound of each of the metals or elements so as to provide the desired ratios of the

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metals or elements in the catalyst composition. One specific preferred metal precursor is a Ta precursor that is prepared by slowly hydrolyzing tantalum ethoxide in oxalic acid and water and then diluting making a tantalum oxalate. This process works particularly well for group 5 metals, such as Ta and Nb and is preferred because it provides a soluble Ta or Nb precursor, it is

5   chloride free and generally provides better performance. Previous Ta solutions included chloride, which is not desirable generally. Details of specific metal precursors are disclosed in the examples. A metal precursor solution or suspension may be prepared for each metal or element in the desired catalyst composition, or a single metal precursor solution may include multiple metals or elements. After mixing the metal precursors, the solvent is driven off by any

10   one a variety of techniques known to those of skill in the art, such as evaporation, freeze drying, etc. Thereafter, the composition is calcinated. Calcination is typically carried out at a temperature in the range of from about 200°C to about 1000°C. Preferred calcination temperatures are less than 600°C or less than 500°C and greater than 250°C or greater than 300°C. Calcination of the samples can be for ½ hour to 24 hours, more specifically from 1 to 12

15   hours and even more specifically from about 1 to 6 hours. Calcination may be carried out in an atmosphere of air. Preferably, there is a ramp up in the calcination temperature, as disclosed in the examples.

Choice of calcination conditions can affect the activity of the catalyst depending on the catalyst composition and dehydrogenation reaction conditions. For example, by lowering the

20   calcination temperature, Ni-Nb-Ta oxides are generally more active for catalyzing ethane oxidative dehydrogenation at low temperature with higher conversions. As specifically shown in the examples, a calcination temperature for Ni-Nb-Ta oxides of about 400°C gave generally lower conversions in comparison to a calcination temperature of about 300°C.

One preferred method is an aqueous method where various aqueous solutions comprised

25   of water-soluble metal precursors are combined in proper volumetric ratios to obtain mixtures having desired metal compositions. Next, water is separated from the mixtures by lyophilization or precipitation. Lyophilization refers to freezing the resulting mixture under liquid nitrogen, and then placing the mixture in a high vacuum so that the water (ice) sublimes, leaving behind mixtures of dry metal precursors. Precipitation refers to separating dissolved metal ions by

30   adding one or more chemical reagents that will precipitate sparingly soluble salts of the metal

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ions. Such chemical reagents may provide ions that shift ionic equilibria to favor formation of insoluble metal salts (common ion effect), or may bind with metal ions to form uncharged, insoluble coordination compounds (complexation). In addition, such reagents may oxidize or reduce metal ions to form ionic species that produce insoluble salts. Other precipitation

5 mechanisms include hydrolysis, in which metal ions react with water in the presence of a weak base to form insoluble metal salts. Whatever the mechanism, the precipitate is separated from the remaining solution by first centrifuging the solutions and then decanting the supernatant; residual water can be removed by heating the precipitates or in vacuum. Finally, whether prepared by the sol-gel method or by the aqueous methods, the dry mixtures are calcined and

10 may be ground to ensure a consistent bulk density among samples.

In addition, the usefulness of the catalysts of this invention is not necessarily limited to dehydrogenation reactions. Other useful reactions that may be performed with the catalysts include selective oxidation, ammoxidation, amination, homo and cross carbon-carbon coupling, dimerization and isomerization reactions.

EXAMPLES

The following examples are intended as illustrative and non-limiting, and represent specific embodiments of the present invention.

Example 1.   Ni-Co-Nb Oxide Mixtures

20 Catalysts were prepared by an aqueous method. One molar nickel and 1.0 M cobalt stock solutions were prepared by dissolving 29.088 g of nickel (II) nitrate hexahydrate in distilled water to a final volume of 100 ml and by dissolving 29.129 g of cobalt (II) nitrate hexahydrate in distilled water to a final volume of 100 ml, respectively. A 1.0 M niobium stock solution was prepared by slowly hydrolyzing 100 mmol niobium ethoxide in an oxalic acid solution (2.7 M) in

25 distilled water at 60°C and diluted to 100 ml in volume after cooling to 25°C. A CAVRO automated liquid dispensing system was used to deliver aliquots of the aqueous stock solutions

into 28 vessels. Each vessel contained 2250 µl of solution, and the molar concentrations of the metal ions in each vessel were given by expressions:

$$[Ni]_{i,j} = \frac{2000 - 300(i-1)}{2250}, \quad M \qquad\qquad IV$$

$$[Co]_{i,j} = \frac{200 + 300(j-1)}{2250}, \quad M \qquad\qquad V$$

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$$[Nb]_{i,j} = \frac{50 + 75(i-j)}{2250}, \quad M \qquad\qquad VI$$

In expressions IV through VI, subscripts i and j represent row and column indices of a 7-by-7 triangular array, respectively, and $i \geq j$, $i = 1,\ldots,7$, and $j = 1,\ldots,7$.

Water was separated from the mixtures by lyophilization (freeze drying). Each of the 28 aqueous solutions were frozen under liquid nitrogen, and then placed in a high vacuum to

10 vaporize the ice. The resulting dry mixtures were placed in an oven for calcination. The temperature of the oven was increased from room temperature to 120 °C at a rate of 1 °C/min. The oven temperature was maintained at 120 °C for 2 hours, and was then ramped at 1 °C/min. to 180 °C. The oven temperature was held at 180 °C for 2 hours and was then ramped at 2 °C/min. to 400 °C. After 8 hours at 400 °C, the oxide mixtures were removed from the oven and

15 were allowed to cool to room temperature. The bulk samples were ground with a spatula to ensure consistent bulk density.

The catalyst compositions were each contacted with a gas mixture comprised of ethane and oxygen and by measuring the composition of the gas mixture following contact with the bulk samples. The best performing catalysts were those that yielded the highest ethane conversion

20 and ethylene selectivity. Contacting was carried out in a 48-vessel parallel fixed bed reactor as described in U.S. Patent Application No. 09/093,870, "Parallel Fixed Bed Reactor and Fluid Contacting Apparatus and Method," filed June 9, 1998, which is incorporated herein by reference.

Table 1 lists the composition and mass of Ni-Co-Nb oxide mixtures tested. High purity

25 ethane and 14.4 % O_2 in N_2 were obtained from MATHESON. Pure N_2 was obtained from an

in-house supply line. After loading the reactor vessels with the 28 catalysts, the vessels were

purged with N_2 to remove residual O_2. Next, the vessels were purged with ethane for another ten

minutes. The composition of the effluent from each of the vessels was measured by gas

chromatography (GC) to ensure that the ethane level had reached 95 % prior to screening. The

5   O_2/N_2 mixture was then added so that the reactant flow rate was 0.524 sccm per minute per

reactor vessel, and the reactant gas composition was 40.1 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Gas

flow stability was measured periodically by GC. Two VARIAN 3800, 3-channel gas

chromatographs were used to detect ethylene in vessel effluent. Each of the three channels

contained 6-inch HAYESEP columns, methanizers, and flame-ionization detectors. CO, CO_2,

10   C_2H_4, and C_2H_6 were separated to baseline in about three minutes. The responses of the flame

ionization detectors and the methanizers were calibrated using a standard gas mixture containing

2.0 % CO, 2.0 % CO_2, 6.0 % C_2H_4, 30.0 % C_2H_6, 4.0 % O_2 and the balance N_2. Five calibration

experiments were carried out to generate calibration coefficients. Reactor (vessel) temperature

was maintained at 300 °C, and reactions were carried out at 15 psia. Tables 2 and 3 list ethane

15   conversion and ethylene selectivity, respectively, for each of the Ni-Co-Nb oxide mixtures listed

in Table 1.

Example 2.   Ni-Co-Nb Oxide Mixtures

         Table 4 lists composition and mass of Ni-Co-Nb oxides belonging to a second library.

Like the bulk samples described in Example 1, the oxide mixtures shown in Table 4 were

20   prepared from aqueous stock solutions of nickel (II) nitrate hexahydrate, cobalt (II) nitrate

hexahydrate and niobium (V) oxalate. A CAVRO automated liquid dispensing system was used

to deliver aliquots of the aqueous stock solutions into vessels. Water was separated from the

mixtures by lyophilization, and the resulting dry mixtures were placed in an oven to oxidize the

metal precursors in accordance with the temperature-time profile described in Example 1. The

25   bulk samples were ground with a spatula to ensure consistent bulk density, and were evaluated

for catalytic performance by contacting each sample with ethane and oxygen in a parallel fixed

bed reactor. Reaction conditions were the same as those used to evaluate the mixed oxides

shown in Table 1 of Example 1. Table 5 and 6 list ethane conversion and ethylene selectivity at

300 °C, respectively, for each of the Ni-Co-Nb oxide mixtures listed in Table 4.

Example 3.   Ni-Co-Nb Oxide Mixtures

Table 7 lists composition and mass of Ni-Co-Nb oxides belonging to a third library. Like

the bulk samples described in Example 1, the oxide mixtures shown in Table 7 were prepared

from aqueous stock solutions of nickel (II) nitrate hexahydrate, cobalt (II) nitrate hexahydrate

5   and niobium (V) oxalate. A CAVRO automated liquid dispensing system was used to deliver

aliquots of the aqueous stock solutions into vessels. Water was separated from the mixtures by

lyophilization, and the resulting dry mixtures were placed in an oven to oxidize the metal

precursors in accordance with the temperature-time profile described in Example 1. The bulk

samples were ground with a spatula to ensure consistent bulk density, and were evaluated for

10   catalytic performance in ODHE by contacting each sample with ethane and oxygen in a parallel

fixed bed reactor. Reaction conditions were the same as those used to evaluate the mixed oxides

shown in Table 1 of Example 1, except that the reactant flow rate was 1.048 sccm per minute per

vessel. Table 8 and 9 list ethane conversion and ethylene selectivity at 300 °C, respectively, for

each of the Ni-Co-Nb oxide mixtures listed in Table 7.

15   Example 4.   Ni-Co-Nb Oxide Mixtures

66 bulk samples of Ni-Co-Nb oxide mixtures were prepared and tested. The

compositions of the oxide mixtures, which are listed in Table 10, encompassed a full range of

ternary mixtures. Like the bulk samples described in Example 1, the oxide mixtures shown in

Table 10 were prepared from aqueous stock solutions of nickel (II) nitrate hexahydrate, cobalt

20   (II) nitrate hexahydrate and niobium (V) oxalate. A CAVRO automated liquid dispensing

system was used to deliver aliquots of the aqueous stock solutions into vessels. The samples

were lyophilized, calcined and ground in a manner similar to the mixed oxides shown in Table 1

of Example 1, and were evaluated for catalytic performance by contacting each sample with

ethane and oxygen in a parallel fixed bed reactor. Reaction conditions were the same as those

25   used to evaluate the mixed oxides shown in Table 7 of Example 3. Tables 11 and 12 list ethane

conversion and ethylene selectivity at 300 °C, respectively, for each of the Ni-Co-Nb oxide

mixtures listed in Table 12.

Example 5.   Ni-Co-Nb Oxide Mixtures

Table 13 lists composition and mass of Ni-Co-Nb oxides belonging to a fourth library. Like the bulk samples described in Example 1, the oxide mixtures shown in Table 13 were prepared from 1.0 M nickel (II) nitrate hexahydrate, 1.0 M cobalt (II) nitrate hexahydrate and 1.0

5   M niobium (V) oxalate aqueous stock solutions. A CAVRO automated liquid dispensing system was used to deliver aliquots of the aqueous stock solutions into vessels. Each vessel contained about 1.9 ml of solution. In contrast to Example 1, the metal precursors were separated from the aqueous phase by precipitation. One ml of ammonium hydroxide (28% ammonia in water) was added to each of the solutions resulting in a solid precipitate. The solid precipitate was separated

10   from the aqueous phase by centrifuging at 4000 rpm for 20 minutes, followed by decanting the supernatant. The solid was dried in a vacuum oven at 60 °C for about an hour, and then calcined in accordance with the temperature-time profile described in Example 1. The bulk samples were ground with a spatula to ensure consistent bulk density, and were evaluated for catalytic performance in ODHE by contacting each sample with ethane and oxygen in a parallel fixed bed

15   reactor. Reaction conditions were the same as those used to evaluate the mixed oxides shown in Table 7 of Example 3. Table 14 and 15 list ethane conversion and ethylene selectivity at 300 °C, respectively, for each of the Ni-Co-Nb oxide mixtures listed in Table 13.

Example 6.   Ni-Nb and Ni-Co-Nb Oxide Mixtures: Effect of Sample Mass, Reaction
                      Temperature and Oxygen Content of Reactor Feed on Ethane Conversion and

20   Selectivity; Comparison with Optimized Mo-V-Nb Oxide Catalyst

Fig. 1 illustrates ethane conversion and ethylene selectivity as a function of reaction temperature for two of the catalysts in Table 13 of Example 5—$Ni_{0.63}Nb_{0.37}$ and $Ni_{0.55}Nb_{0.45}$—as well as an optimized Mo-V-Nb catalyst. The catalysts were evaluated in a parallel fixed bed reactor at temperatures ranging from 250 °C to 350 °C. The Ni-Nb catalysts were tested at two

25   different sample masses, while the Mo-V-Nb catalyst was tested at three different sample masses. Reactant flow rate was 1.048 sccm per minute per reactor vessel (sample), and the reactant gas was comprised of 40.1 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Ethane conversion curves are shown for $Ni_{0.63}Nb_{0.37}$ (10.0 mg, 37.0 mg) 202, 204; $Ni_{0.55}Nb_{0.45}$ (16.4 mg, 48.9 mg) 206, 208; and Mo-V-Nb (12.3 mg, 23.4 mg, 72.2 mg) 210, 212, 214. Ethylene selectivity curves are

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shown for $Ni_{0.63}Nb_{0.37}$ (10.0 mg, 37.0 mg) 216, 218; $Ni_{0.55}Nb_{0.45}$ (16.4 mg, 48.9 mg) 220, 222; and Mo-V-Nb (12.3 mg, 23.4 mg, 72.2 mg) 224, 226, 228.

Fig. 2 illustrates ethane conversion and ethylene selectivity as a function of oxygen content of the reactor feed for the two Ni-Nb catalysts and the optimized Mo-V-Nb catalyst. The catalysts were evaluated in the parallel fixed bed reactor at 300 °C. As in Fig. 2, the Ni-Nb catalysts were tested at two different sample masses, and the Mo-V-Nb catalyst was tested at three different sample masses. In all cases, reactant flow rate was 1.048 sccm per minute per reactor vessel (sample). The reactant feed was comprised of 0 % to 21 % O_2, 51.5 % N_2, and the balance C_2H_6. Ethane conversion curves are shown for $Ni_{0.63}Nb_{0.37}$ (10.0 mg, 37.0 mg) 302, 304; $Ni_{0.55}Nb_{0.45}$ (16.4 mg, 48.9 mg) 306, 308; and Mo-V-Nb (12.3 mg, 23.4 mg, 72.2 mg) 310, 312, 314. Ethylene selectivity curves are shown for $Ni_{0.63}Nb_{0.37}$ (10.0 mg, 37.0 mg) 316, 318; $Ni_{0.55}Nb_{0.45}$ (16.4 mg, 48.9 mg) 320, 322; and Mo-V-Nb (12.3 mg, 23.4 mg, 72.2 mg) 324, 326, 328.

Fig. 3 illustrates ethane conversion and ethylene selectivity as a function of the amount of oxygen in the reactor feed for four catalysts shown in Table 13 that contain small amounts of cobalt—$Ni_{0.81}Co_{0.04}Nb_{0.16}$, $Ni_{0.65}Co_{0.04}Nb_{0.31}$, $Ni_{0.58}Co_{0.04}Nb_{0.39}$ and $Ni_{0.60}Co_{0.08}Nb_{0.32}$. For comparison, Fig. 3 also shows ethane conversion and ethylene selectivity for the optimized Mo-V-Nb catalyst. The catalysts were evaluated in the parallel fixed bed reactor at 300 °C. The Ni-Co-Nb catalysts were each tested at one sample mass, and the Mo-V-Nb catalyst was tested at three different sample masses. In all cases, reactant flow rate was 1.048 sccm per minute per reactor vessel (sample). The reactant feed was comprised of 0 % to 21 % O_2, 51.5 % N_2, and the balance C_2H_6. Ethane conversion curves are shown for $Ni_{0.81}Co_{0.04}Nb_{0.16}$ (35.8 mg) 402; $Ni_{0.65}Co_{0.04}Nb_{0.31}$ (32.4 mg) 404; $Ni_{0.58}Co_{0.04}Nb_{0.39}$ (38.3 mg) 406; $Ni_{0.60}Co_{0.08}Nb_{0.32}$ (30.2 mg) 408; and Mo-V-Nb (12.3 mg, 23.4 mg, 72.2 mg) 410, 412, 414. Ethylene selectivity curves are shown for $Ni_{0.81}Co_{0.04}Nb_{0.16}$ (35.8 mg) 416; $Ni_{0.65}Co_{0.04}Nb_{0.31}$ (32.4 mg) 418; $Ni_{0.58}Co_{0.04}Nb_{0.39}$ (38.3 mg) 420; $Ni_{0.60}Co_{0.08}Nb_{0.32}$ (30.2 mg) 422; and Mo-V-Nb (12.3 mg, 23.4 mg, 72.2 mg) 424, 426, 428.

Example 7.   Ni-Nb-Ta-K Oxide Mixtures

        Table 16 lists composition and mass of a focused Ni-Nb-Ta-K oxide library. The oxide

mixtures were selected based on the primary screening results shown in Table 21 and were

prepared from 1.0 M nickel (II) nitrate hexahydrate, 0.70 M niobium (V) oxalate, 0.87 M

5   tantalum oxalate and 1.07 M potassium nitrate aqueous stock solutions. A CAVRO automated

liquid dispensing system was used to deliver aliquots of the aqueous stock solutions into vessels.

Water was separated from the mixtures by lyophilization, and the resulting dry mixtures were

placed in an oven to oxidize the metal precursors in accordance with the temperature-time profile

described in Example 1. The bulk samples were ground with a spatula to ensure consistent bulk

10   density, and were evaluated for catalytic performance in ODHE by contacting each sample with

ethane and oxygen in the parallel fixed bed reactor. Reactant flow rate was 1.048 sccm per

minute per reactor vessel (sample), and the reactant gas was comprised of 40.1 % C_2H_6, 8.4 %

O_2 and 51.5 % N_2. Tables 17 and 18 list ethane conversion and ethylene selectivity at 300 °C,

respectively, for each of the Ni-Nb-Ta-K oxide mixtures listed in Table 16.

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Example 8.   Ni- Nb-Ta Oxide Mixtures

        Table 19 lists composition and mass of a Ni-Nb-Ta oxide library. Bulk samples of the

oxide mixtures shown in Table 19 were prepared from 1.0 M nickel (II) nitrate hexahydrate, 1.0

M niobium (V) oxalate and 1.0 M tantalum oxalate aqueous stock solutions. A CAVRO

20   automated liquid dispensing system was used to deliver aliquots of the aqueous stock solutions

into vessels. Each vessel contained about 1.9 ml of solution. Like Example 5, the metal

precursors were separated from the aqueous phase by precipitation. One ml of ammonium

hydroxide (28% ammonia in water) was added to each of the solutions resulting in a solid

precipitate. The solid precipitate was separated from the aqueous phase by centrifuging at 4000

25   rpm for 20 minutes, followed by decanting the supernatant. The solid was dried in a vacuum

oven at 60 °C for about an hour, and then calcined in accordance with the temperature-time

profile described in Example 1. The bulk samples were ground with a spatula to ensure

consistent bulk density, and were evaluated for catalytic performance in ODHE by contacting

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each sample with ethane and oxygen in a parallel fixed bed reactor. Reactant flow rate was 1.048 sccm per minute per reactor vessel (sample), and the reactant gas was comprised of 40.1 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Tables 20 and 21 list ethane conversion and ethylene selectivity at 300 °C, respectively, for each of the Ni-Nb-Ta oxide mixtures listed in Table 19.

5   Example 9.   Ni- Nb-Ta Oxide Mixtures: Ethylene in Reactor Feed

Table 22 lists composition and mass of a Ni-Nb-Ta oxide library. The oxide mixtures shown in Table 22 were prepared from 1.0 M nickel (II) nitrate hexahydrate, 1.0 M niobium (V) oxalate and 1.0 M tantalum oxalate aqueous stock solutions, as disclosed above. A CAVRO automated liquid dispensing system was used to deliver aliquots of the aqueous stock solutions into vessels. Each vessel contained about 3.3 ml of solution. The metal precursors were from the aqueous phase by precipitation. About 2.9 ml of a 1.57 M ammonium carbonate solution was added to each of the solutions resulting in a solid precipitate. The solid precipitate was separated from the aqueous phase by centrifuging at 4000 rpm for 20 minutes, followed by decanting the supernatant. The solid was dried in a vacuum oven at 60 °C for about an hour, and then calcined in accordance with the temperature-time profile described in Example 1. The bulk samples were ground with a spatula to ensure consistent bulk density, and were evaluated for catalytic performance in ODHE by contacting each sample with ethane and oxygen in a parallel fixed bed reactor. Reactant flow rate was 1.048 sccm per minute per reactor vessel (sample), and the reactant gas was comprised of 40.1 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Table 23 and 24 list ethane conversion and ethylene selectivity at 300 °C, respectively, for each of the Ni-Nb-Ta oxide mixtures listed in Table 22. Table 25 and 26 list ethane conversion and ethylene selectivity at 325 °C.

To determine the effect of ethylene in the reactor feed on ethane conversion and ethylene selectivity, the mixed oxide samples listed in Table 22 were contacted with a gas mixture comprised of 11.2 % C_2H_4, 28.1 % C_2H_6, 0.8 % CO_2, 8.4 % O_2 and 51.5 % N_2. Reactant flow rate was maintained at 1.048 sccm per minute per reactor vessel (sample), and the fractions of C_2H_4, C_2H_6 and CO_2 in the reactor feed were verified during screening by measuring the composition of gas effluent from blank vessels in the parallel fixed bed reactor. Tables 27 and 28, which list changes in ethane and ethylene concentration following contact with the Ni-Nb-Ta

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oxide mixtures, show significant ethane conversion to ethylene at 325 °C. Table 29 lists CO and CO_2 production at 325 °C.

Example 10.   Ni-Nb-Ta Oxide Mixtures: Ethylene in Reactor Feed

Table 30 lists composition and mass of another Ni-Nb-Ta oxide library. The oxide

5   mixtures shown in Table 30 were prepared from 1.0 M nickel (II) nitrate hexahydrate, 1.0 M niobium (V) oxalate and 1.0 M tantalum oxalate aqueous stock solutions. A CAVRO automated liquid dispensing system was used to deliver aliquots of the aqueous stock solutions into vessels. Each vessel contained about 3.3 ml of solution. The metal precursors were separated from the aqueous phase by precipitation. About 2.9 ml of a 1.57 M ammonium carbonate solution was

10   added to each of the solutions resulting in a solid precipitate. The solid precipitate was separated from the aqueous phase by centrifuging at 4000 rpm for 20 minutes, followed by decanting the supernatant. The solid was dried in a vacuum oven at 60 °C for about an hour, and then calcined in accordance with the temperature-time profile described in Example 1. The bulk samples were ground with a spatula to ensure consistent bulk density, and were evaluated for catalytic

15   performance in ODHE by contacting each sample with ethane and oxygen in a parallel fixed bed reactor. Reactant flow rate was 1.048 sccm per minute per reactor vessel (sample), and the reactant gas was comprised of 40.1 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Table 31 and 32 list ethane conversion and ethylene selectivity at 300 °C, respectively, for each of the Ni-Nb-Ta oxide mixtures listed in Table 30. Table 33 and 34 list ethane conversion and ethylene

20   selectivity at 325 °C.

To determine the effect of ethylene in the reactor feed on ethane conversion and ethylene selectivity, the mixed oxide samples listed in Table 30 were contacted with a gas mixture comprised of 11.2 % C_2H_4, 28.5 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Reactant flow rate was maintained at 1.048 sccm per minute per reactor vessel (sample), and the fractions of C_2H_4, C_2H_6

25   and CO_2 in the reactor feed were verified during screening by measuring the composition of gas effluent from blank vessels in the parallel fixed bed reactor. Tables 35 and 36, which list changes in ethane and ethylene concentration following contact with the Ni-Nb-Ta oxide mixtures, show significant ethane conversion to ethylene at 325 °C. Table 37 lists CO and CO_2 production at 325 °C.

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Example 11.   Ni- Nb-Ta Oxide Mixtures at Lower Calcination Temperature

Table 38 lists composition and mass of a Ni-Nb-Ta oxide library. Bulk samples of the oxide mixtures shown in Table 38 were prepared from 1.0 M nickel (II) nitrate hexahydrate, 1.0 M niobium (V) oxalate and 1.0 M tantalum oxalate aqueous stock solutions. A CAVRO

5   automated liquid dispensing system was used to deliver aliquots of the aqueous stock solutions into vessels. Each vessel contained about 1.9 ml of solution. Like Example 5, the metal precursors were separated from the aqueous phase by precipitation. Ammonium carbonate (1.62 M) was added to each of the solutions resulting in a solid precipitate. The mixture was allowed to settle at 25°C for 3 hours. The solid precipitate was separated from the aqueous phase by

10   centrifuging at 4000 rpm for 10 minutes, followed by decanting the supernatant. The solid was dried in a vacuum oven at 60°C for about an hour. The solid obtained was calcined in air under the following temperature-time profile: The temperature of the oven was increased from room temperature to 300°C at a rate of 2°C/min. The oven temperature was held at 300°C for 8 hours. After 8 hours at 300°C, the oxide mixtures were removed from the oven and were allowed to

15   cool to room temperature. The bulk samples were ground with a spatula to ensure consistent bulk density. The bulk samples were evaluated for catalytic performance by contacting each sample with ethane and oxygen in a parallel fixed bed reactor, described in Example 1. Reactant flow rate was 1.048 sccm per minute per reactor vessel (sample), and the reactant gas was comprised of 40.1 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Tables 39 and 40 list ethane conversion

20   and ethylene selectivity at 300 °C, respectively, for each of the Ni-Nb-Ta oxide mixtures listed in Table 38. The ethane dehydrogenation reaction was also carried out at 250°C and Tables 41 and 42 list ethane conversion and ethylene selectivity at 250°C, respectively, for each of the Ni-Nb-Ta oxide mixtures listed in Table 38.

To determine the effect of ethylene in the reactor feed on ethane conversion and ethylene

25   selectivity, selected mixed oxide samples listed in Table 38 were contacted in the parallel fixed bed reaction with a gas mixture comprised of 11.3 % C_2H_4, 28.7 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Reactant flow rate was maintained at 1.048 sccm per minute per reactor vessel (sample), and the fractions of C_2H_4, C_2H_6 and CO_2 in the reactor feed were verified during screening by measuring the composition of gas effluent from blank vessels in the parallel fixed bed reactor.

30   Tables 43 and 44, which list the selected samples as well as changes in ethane and ethylene

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concentration following contact with the Ni-Nb-Ta oxide mixtures, show significant ethane conversion to ethylene at 300 °C. Table 45 lists CO_2 production at 300 °C. The test was repeated at 275°C for the same selected samples.

Example 12.   Ni-Nb, Ni-Co, Ni-Co-Nb, Ni-Nb-Al, Ni-Nb-Fe and Optimized Mo-V-Nb Oxide

5   Mixtures: Ethylene in Reactor Feed

Table 46 lists composition and mass of Ni-Nb, Ni-Co, Ni-Co-Nb, Ni-Nb-Al and Ni-Nb-Fe oxide mixtures, as well as an optimized Mo-V-Nb oxide catalyst. Bulk samples of each of these oxide mixtures were prepared using aqueous methods described above. For the Ni-Nb-Al and Ni-Nb-Fe oxide mixtures, methods similar to those of Example 5 were followed except that

10   1.0M aluminum nitrate and 1.0M ferric nitrate, were used, respectively. Bulk samples were evaluated for catalytic performance in ODHE by contacting each sample with ethane, ethylene and oxygen in the parallel fixed bed reactor. The reactant gas was comprised of 11.6 % C_2H_4, 28.5 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Reactant flow rate was maintained at 1.048 sccm per minute per reactor vessel (sample), and fractions of C_2H_4 and C_2H_6 in the reactor feed were

15   verified during screening by measuring the composition of gas effluent from blank vessels in the parallel fixed bed reactor. Table 46, which also lists changes in ethane and ethylene concentration following contact with the oxide mixtures, shows significant ethane conversion to ethylene for many of the mixed oxides. Notable exceptions include two of the Mo-V-Nb oxide samples.

20   Example 13.   Ni- Nb Oxide Mixtures: Effect of Preparation on Performance

To gauge the influence of the bulk sample preparation method on catalyst performance, Ni-Nb oxide compositions were prepared using six different reagents to precipitate the metal precursors. The reagents include ammonium hydroxide, tetraethylammonium hydroxide, potassium carbonate, sodium hydroxide, potassium hydroxide, and ammonium carbonate, as

25   follows: **Ammonium hydroxide:** 1.0 ml of ammonium hydroxide (28% ammonia in water) was added to a solution of nickel nitrate (1.0M, 1.29 ml), niobium oxalate (1.07M, 0.57 ml), and Cobalt (II) nitrate (0.07 ml, 1.0M). The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. The solid was dried in a vacuum oven at 60°C and then calcined at a maximum temperature of 400°C. **Ammonium carbonate:** 2.9 ml of ammonium

carbonate (1.57M) was added to a solution of nickel nitrate (1.0M, 1.53 ml), niobium oxalate (0.52M, 0.87 ml), and Tantalum oxalate (0.87 ml, 0.52M). Foam (CO_2) was formed accompanied with the formation of a solid. The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. To the solid, about 5 ml of distilled water was

5   added and then mixed. The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. The solid was dried in a vacuum oven at 60°C and then calcined at a maximum temperature of 400°C. **Tetraethylammonium hydroxide:** 4.4 ml of tetraethylamminium hydroxide (1.14M) was added to a solution of nickel nitrate (1.0M, 2.60 ml) and niobium oxalate (0.70M, 0.70 ml). The resulting mixture was centrifuged at 4000 rpm for

10 20 minutes and the solution was decanted. To the solid, about 5 ml of distilled water was added and then mixed. The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. The solid was dried in a vacuum oven at 60°C and then calcined at a maximum temperature of 400°C. **Potassium hydroxide:** 0.6 ml of potassium hydroxide (5.26M in water) was added to a solution of nickel nitrate (1.0M, 1.50 ml) and niobium oxalate (0.70M,

15 0.30 ml). The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. To the solid, about 5 ml of distilled water was added and then mixed. The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. The solid was dried in a vacuum oven at 60°C and then calcined at a maximum temperature of 400°C. **Sodium hydroxide:** 1.0 ml of sodium hydroxide (3.0M in water) was added to a

20 solution of nickel nitrate (1.0M, 1.50 ml) and niobium oxalate (0.7M, 0.30 ml). The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. To the solid, about 5 ml of distilled water was added and then mixed. The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. The solid was dried in a vacuum oven at 60°C and then calcined at a maximum temperature of 400°C. **Potassium carbonate:** 1.5

25 ml of potassium carbonate (2.04M in water) was added to a solution of nickel nitrate (1.0M, 1.50 ml) and niobium oxalate (0.70M, 0.30 ml). The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. To the solid, about 5 ml of distilled water was added and then mixed. The resulting mixture was centrifuged at 4000 rpm for 20 minutes and the solution was decanted. The solid was dried in a vacuum oven at 60°C and then calcined at a

30 maximum temperature of 400°C. Table 47 lists the compositions of the Ni-Nb oxide mixtures,

which were evaluated for catalytic performance in ODHE by contacting each sample with ethane and oxygen in a parallel fixed bed reactor. Reactant flow rate was 1.048 sccm per minute per reactor vessel (sample), and the reactant gas was comprised of 40.1 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Tables 48 and 49 list ethane conversion and ethylene selectivity at 300 °C, respectively, for each of the Ni-Nb oxide mixtures prepared using the six different reagents.

Example 14.   Ni-Ta Oxide Mixtures

Table 50 lists composition and mass of a Ni-Ta oxide library. The oxide mixtures were prepared from 1.0 M nickel (II) nitrate hexahydrate and 1.0 M tantalum oxalate aqueous stock solutions. A CAVRO automated liquid dispensing system was used to deliver aliquots of the aqueous stock solutions into vessels. Each vessel contained about 3.3 ml of solution. About 1.1 ml of a 1.14 M tetraethylammonium hydroxide solution was added to each of the solutions resulting in a solid precipitate. The solid precipitate was separated from the aqueous phase by centrifuging at 4000 rpm for 20 minutes, followed by decanting the supernatant. The solid was dried in a vacuum oven at 60 °C for about an hour, and then calcined in accordance with the temperature-time profile described in Example 1. The bulk samples were ground with a spatula to ensure consistent bulk density, and were evaluated for catalytic performance in ODHE by contacting each sample with ethane and oxygen in a parallel fixed bed reactor. Reactant flow rate was 1.048 sccm per minute per reactor vessel (sample), and the reactant gas was comprised of 40.1 % C_2H_6, 8.4 % O_2 and 51.5 % N_2. Table 50 lists ethane conversion and ethylene selectivity at 300 °C for each of the Ni-Ta oxide mixtures

It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should therefore be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated herein by reference for all purposes.

Table 1. Composition and mass of Ni-Co-Nb oxide mixtures

		1	2	3	4	5	6	7
		Mole Fraction & Sample Mass, mg						
1	Ni	0.89						
	Co	0.09						
	Nb	0.02						
	M	59.3						
2	Ni	0.84	0.76					
	Co	0.10	0.22					
	Nb	0.06	0.02					
	M	35.5	59.5					
3	Ni	0.78	0.69	0.62				
	Co	0.11	0.25	0.36				
	Nb	0.11	0.06	0.02				
	M	31.4	39.7	49.4				
4	Ni	0.70	0.61	0.54	0.49			
	Co	0.13	0.28	0.40	0.49			
	Nb	0.17	0.11	0.06	0.02			
	M	50.5	43.3	36.0	52.4			
5	Ni	0.59	0.51	0.44	0.40	0.36		
	Co	0.15	0.32	0.44	0.54	0.62		
	Nb	0.26	0.17	0.11	0.06	0.02		
	M	46.9	48.6	33.8	52.3	48.9		
6	Ni	0.44	0.37	0.32	0.28	0.25	0.22	
	Co	0.18	0.37	0.51	0.61	0.69	0.76	
	Nb	0.38	0.26	0.17	0.11	0.06	0.02	
	M	43.9	46.7	46.7	36.1	42.1	62.9	
7	Ni	0.22	0.18	0.15	0.13	0.11	0.10	0.09
	Co	0.22	0.44	0.59	0.70	0.78	0.84	0.89
	Nb	0.56	0.38	0.26	0.17	0.11	0.06	0.02
	M	45.8	46.8	47.3	50.7	45.7	65.4	48.5

Table 2. Ethane conversion of Ni-Co-Nb oxide mixtures listed in Table 1

	1	2	3	4	5	6	7
	Ethane Conversion, %						
1	17.6						
2	16.3	10.4					
3	15.0	10.1	11.8				
4	17.1	10.9	11.2	10.0			
5	11.5	12.4	11.7	10.4	11.2		
6	12.3	11.5	13.3	10.9	11.7	12.6	
7	9.6	11.5	9.3	12.4	11.7	11.8	10.9

Table 3. Ethylene selectivity of Ni-Co-Nb oxide mixtures listed in Table 1

	1	2	3	4	5	6	7
	Ethylene Selectivity, %						
1	40.7						
2	39.4	45.6					
3	46.8	42.1	31.6				
4	61.3	48.5	29.8	31.9			
5	48.0	34.0	34.0	35.5	30.9		
6	36.7	29.8	32.3	36.3	33.9	35.2	
7	30.6	30.5	38.9	35.3	32.6	33.2	37.4

Table 4. Composition and mass of Ni-Co-Nb oxide mixtures

		1	2	3	4	5	6
		Mole Fraction & Sample Mass, mg					
1	Ni	0.73	0.71	0.69	0.67	0.65	0.63
	Co	0.03	0.06	0.09	0.12	0.15	0.17
	Nb	0.23	0.23	0.22	0.21	0.21	0.20
	M	43.7	45.8	47.2	45.8	44.0	50.1.
2	Ni	0.76	0.73	0.71	0.60	0.67	0.65
	Co	0.03	0.07	0.10	0.13	0.15	0.18
	Nb	0.21	0.20	0.19	0.19	0.18	0.18
	M	44.3	44.0	48.5	42.9	43.6	47.1
3	Ni	0.79	0.76	0.73	0.71	0.69	0.67
	Co	0.04	0.07	0.10	0.13	0.16	0.18
	Nb	0.18	0.17	0.17	0.16	0.16	0.15
	M	43.1	44.7	47.7	46.0	50.4	46.9
4	Ni	0.81	0.79	0.76	0.73	0.71	0.69
	Co	0.04	0.07	0.10	0.13	0.16	0.19
	Nb	0.14	0.14	0.14	0.13	0.13	0.13
	M	42.8	41.4	44.6	42.8	44.5	43.1

5   Table 5. Ethane conversion of Ni-Co-Nb oxide mixtures listed in Table 4

	1	2	3	4	5	6
	Ethane Conversion, %					
1	22.8	16.4	16.8	13.6	13.3	13.5
2	21.4	16.2	19.5	15.9	14.6	14.9
3	22.7	15.7	16.9	15.4	15.5	15.0
4	17.3	14.0	15.6	14.5	13.9	15.0

Table 6. Ethylene selectivity of Ni-Co-Nb oxide mixtures listed in Table 4

	1	2	3	4	5	6
	Ethylene Selectivity, %					
1	62.2	70.1	56.4	52.7	45.8	44.0
2	66.3	69.8	66.1	61.5	. 50.1	46.3
3	64.8	71.7	61.8	60.8	55.7	52.3
4	63.8	69.6	59.8	57.0	51.3	48.0

Table 7. Composition and mass of Ni-Co-Nb oxide mixtures

		1	2	3	4
		Mole Fraction & Sample Mass, mg			
1	Ni	1.00			
	Co	0.00			
	Nb	0.00			
	M	45.6			
2	Ni	0.85	0.84	0.83	0.82
	Co	0.00	0.01	0.02	0.03
	Nb	0.15	0.15	0.15	0.15
	M	40.5	40.3	40.1	41.0
3	Ni	0.81	0.81	0.80	0.79
	Co	0.00	0.01	0.02	0.03
	Nb	0.19	0.18	0.18	0.18
	M	39.2	43.8	41.6	41.6
4	Ni	0.79	0.78	0.77	0.77
	Co	0.00	0.01	0.02	0.03
	Nb	0.21	0.21	0.21	0.21
	M	40.1	40.0	39.2	42.7
5	Ni	0.76	0.75	0.75	0.74
	Co	0.00	0.01	0.02	0.03
	Nb	0.24	0.24	0.24	0.24
	M	39.3	40.9	40.9	39.9
6	Ni	0.73	0.73	0.72	0.72
	Co	0.00	0.01	0.02	0.02
	Nb	0.27	0.26	0.26	0.26
	M	42.7	40.3	41.6	40.3
7	Ni	0.71	0.70	0.70	0.69
	Co	0.00	0.01	0.02	0.02
	Nb	0.29	0.29	0.29	0.28
	M	42.0	41.7	43.6	46.3
8	Ni	0.69			
	Co	0.00			
	Nb	0.31			
	M	42.8			
9	Ni	0.67			
	Co	0.00			
	Nb	0.33			
	M	41.3			
10	Ni	0.65			
	Co	0.00			
	Nb	0.35			
	M	41.4			

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		1	2	3	4
		Mole Fraction & Sample Mass, mg			
11	Ni	0.63			
	Co	0.00			
	Nb	0.37			
	M	40.9			
12	Ni	0.61			
	Co	0.00			
	Nb	0.39			
	M	40.0			
13	Ni	0.59			
	Co	0.00			
	Nb	0.41			
	M	41.8			
14	Ni	0.58			
	Co	0.00			
	Nb	0.42			
	M	40.9			
15	Ni	0.56			
	Co	0.00			
	Nb	0.44			
	M	41.2			
16	Ni	0.55			
	Co	0.00			
	Nb	0.45			
	M	41.8			
17	Ni	0.54			
	Co	0.00			
	Nb	0.46			
	M	40.0			
18	Ni	0.52			
	Co	0.00			
	Nb	0.48			
	M	40.8			
19	Ni	0.50			
	Co	0.00			
	Nb	0.50			
	M	41.5			

Table 8. Ethane conversion of Ni-Co-Nb oxide mixtures listed in Table 7

	1	2	3	4
	Ethane Conversion, %			
1	3.9			
2	8.3	7.8	7.8	7.6
3	10.0	9.7	9.6	10.7
4	10.0	11.9	9.8	11.3
5	10.9	11.2	10.4	11.4
6	9.7	10.9	9.4	11.0
7	8.7	10.0	9.6	11.0
8	9.8			
9	8.1			
10	7.2			
11	6.5			
12	5.7			
13	5.9			
14	5.5			
15	5.5			
16	4.3			
17	4.5			
18	4.4			
19	3.2			

Table 9. Ethylene selectivity of Ni-Co-Nb oxide mixtures listed in Table 7

	1	2	3	4
	Ethylene Selectivity, %			
1	16.2			
2	69.0	68.6	68.2	65.7
3	74.4	65.7	57.4	59.6
4	68.2	61.7	70.3	70.3
5	61.5	67.8	70.8	69.8
6	68.1	69.4	70.6	69.8
7	68.2	66.2	67.0	69.4
8	63.8			
9	68.9			
10	70.0			
11	70.0			
12	70.0			
13	64.5			
14	70.4			
15	72.5			
16	72.2			
17	73.1			
18	68.0			
19	74.7			

Table 10. Compositions of Ni-Co-Nb oxide mixtures

		1	2	3	4	5	6	7	8	9	10	11
		Mole Fraction & Sample Mass, mg										
1	Ni	1.00										
	Co	0.00										
	Nb	0.00										
	M	25.8										
2	Ni	0.90	0.90									
	Co	0.00	0.10									
	Nb	0.10	0.00									
	M	29.5	31.0									
3	Ni	0.80	0.80	0.80								
	Co	0.00	0.10	0.20								
	Nb	0.20	0.10	0.00								
	M	24.6	24.5	34.4								
4	Ni	0.70	0.70	0.70	0.70							
	Co	0.00	0.10	0.20	0.30							
	Nb	0.30	0.20	0.10	0.00							
	M	26.4	37.0	30.3	29.9							
5	Ni	0.60	0.60	0.60	0.60	0.60						
	Co	0.00	0.10	0.20	0.30	0.40						
	Nb	0.40	0.30	0.20	0.10	0.00						
	M	33.1	34.4	35.5	38.8	31.4						
6	Ni	0.50	0.50	0.50	0.50	0.50	0.50					
	Co	0.00	0.10	0.20	0.30	0.40	0.50					
	Nb	0.50	0.40	0.30	0.20	0.10	0.00					
	M	34.4	32.7	30.8	39.4	30.4	35.5					
7	Ni	0.40	0.40	0.40	0.40	0.40	0.40	0.40				
	Co	0.00	0.10	0.20	0.30	0.40	0.50	0.60				
	Nb	0.60	0.50	0.40	0.30	0.20	0.10	0.00				
	M	34.6	37.5	30.1	30.4	34.3	32.3	30.9				
8	Ni	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30			
	Co	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70			
	Nb	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0.00			
	M	42.7	32.9	35.7	29.5	28.6	36.8	38.4	26.9			
9	Ni	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20		
	Co	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80		
	Nb	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0.00		
	M	35.3	40.7	30.8	33.2	31.2	30.3	33.0	29.6	40.7		
10	Ni	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	
	Co	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	
	Nb	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0.00	
	M	34.4	33.2	53.4	32.7	28.8	25.0	22.8	35.6	31.0	25.6	

		1	2	3	4	5	6	7	8	9	10	11
		Mole Fraction & Sample Mass, mg										
11	Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Co	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
	Nb	1.00	0.90	0.80	0.70	0.60	0.50	0.40	.0.30	0.20	0.10	0.00
	M	36.6	31.0	38.7	32.0	45.2	35.1	41.0	37.0	29.1	29.6	29.0

Table 11. Ethane conversion of Ni-Co-Nb oxide mixtures listed in Table 10

	1	2	3	4	5	6	7	8	9	10	11
	Ethane Conversion, %										
1	2.9										
2	5.4	7.1									
3	7.4	7.9	8.3								
4	7.2	11.3	8.6	8.8							
5	5.6	10.2	9.4	8.5	8.1						
6	3.4	9.3	8.5	8.6	7.8	8.1					
7	1.2	7.7	8.4	8.4	8.6	8.9	10.1				
8	0.3	4.2	8.7	8.6	8.4	9.7	8.2	8.1			
9	0.3	15.0	5.5	9.1	7.2	7.4	7.3	7.8	6.9		
10	0.2	1.2	1.5	7.3	7.2	7.3	7.7	8.2	8.4	9.7	
11	0.1	1.4	2.2	3.0	6.1	6.3	6.7	6.7	8.6	6.6	6.7

Table 12. Ethylene selectivity of Ni-Co-Nb oxide mixtures listed in Table 10

	1	2	3	4	5	6	7	8	9	10	11
	Ethylene Selectivity, %										
1	21.0										
2	62.9	33.8									
3	66.9	56.5	36.8								
4	73.6	65.1	44.9	27.9							
5	78.9	53.0	47.5	40.4	31.8						
6	77.6	50.2	38.8	40.4	35.9	30.1					
7	79.7	46.9	35.0	33.5	34.7	34.2	24.7				
8	79.0	45.7	34.2	29.9	30.3	28.1	36.2	32.7			
9	80.3	3.3	32.1	24.4	29.1	31.6	35.2	34.6	34.6		
10	73.4	58.6	51.3	21.4	26.4	27.4	32.9	35.7	34.9	29.4	
11	41.8	27.9	28.5	23.4	19.8	22.5	22.5	22.1	17.1	19.5	17.5

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Table 13. Composition and mass of Ni-Co-Nb oxide mixtures

		1	2	3	4	5	6	7	8
		Mole Fraction & Sample Mass, mg							
1	Ni	1.00							
	Co	0.00							
	Nb	0.00							
	m	44.8							
2	Ni	0.92	0.96						
	Co	0.00	0.04						
	Nb	0.08	0.00						
	m	36.6	34.7						
3	Ni	0.85	0.88	0.92					
	Co	0.00	0.04	0.08					
	Nb	0.15	0.08	0.00					
	m	37.2	33.9	34.1					
4	Ni	0.77	0.81	0.84	0.88				
	Co	0.00	0.04	0.08	0.12				
	Nb	0.23	0.16	0.08	0.00				
	m	40.8	35.8	35.8	42.2				
5	Ni	0.70	0.73	0.76	0.80	0.83			
	Co	0.00	0.04	0.08	0.12	0.17			
	Nb	0.30	0.23	0.16	0.09	0.00			
	m	33.3	38.3	46.8	45.9	20.2			
6	Ni	0.63	0.65	0.68	0.71	0.75	0.78		
	Co	0.00	0.04	0.08	0.12	0.17	0.22		
	Nb	0.37	0.31	0.24	0.17	0.09	0.00		
	m	37.0	32.4	37.7	32.4	48.5	43.0		
7	Ni	0.55	0.58	0.60	0.63	0.66	0.69	0.73	
	Co	0.00	0.04	0.08	0.12	0.16	0.22	0.27	
	Nb	0.45	0.39	0.32	0.25	0.18	0.09	0.00	
	m	48.9	38.3	30.2	32.4	32.5	40.6	36.9	
8	Ni	0.48	0.50	0.52	0.55	0.57	0.60	0.63	0.67
	Co	0.00	0.04	0.07	0.12	0.16	0.21	0.27	0.33
	Nb	0.52	0.46	0.40	0.33	0.26	0.18	0.10	0.00
	m	41.5	36.8	35.8	28.3	37.1	34.5	38.1	40.4

Table 14. Ethane conversion of Ni-Co-Nb oxide mixtures listed in Table 13

	1	2	3	4	5	6	7	8
	Ethane Conversion, %							
1	4.6							
2	2.1	6.5						
3	5.1	4.7	6.9					
4	8.7	11.2	7.2	6.7				
5	9.2	12.1	6.2	8.6	6.5			
6	10.0	13.1	12.9	10.8	8.8	7.2		
7	11.6	14.6	10.1	10.3	8.4	8.0	6.8	
8	7.5	13.2	10.1	8.8	8.7	7.7	9.0	7.4

Table 15. Ethylene selectivity of Ni-Co-Nb oxide mixtures listed in Table 13

	1	2	3	4	5	6	7	8
	Ethylene Selectivity, %							
1	16.7							
2	74.9	32.0						
3	83.8	62.8	35.0					
4	85.1	82.4	54.5	33.5				
5	81.3	84.1	74.3	58.4	31.7			
6	85.3	72.4	79.2	66.7	52.4	29.8		
7	85.7	75.9	68.5	59.7	46.3	37.8	27.2	
8	78.3	76.7	56.9	52.9	50.8	36.3	29.3	31.5

Table 16. Composition and mass of Ni-Nb-Ta-K oxide mixtures

		1	2	3	4	5	6	7
		Mole Fraction & Sample Mass, mg						
1	Ni	0.5837						
	Nb	0.3772						
	Ta	0.0391						
	K	0.0000						
	M	38.7						
2	Ni	0.5910	0.5916					
	Nb	0.3289	0.3292					
	Ta	0.0396	0.0792					
	K	0.0405	0.0000					
	M	35.4	38.4					
3	Ni	0.5985	0.5991	0.5997				
	Nb	0.2793	0.2796	0.2799				
	Ta	0.0401	0.0802	0.1204				
	K	0.0821	0.0411	0.0000				
	M	37.7	38.0	42.0				
4	Ni	0.6062	0.6068	0.6074	0.6080			
	Nb	0.2285	0.2287	0.2290	0.2292			
	Ta	0.0406	0.0812	0.1220	0.1628			
	K	0.1247	0.0832	0.0417	0.0000			
	M	43.1	40.6	38.7	40.8			
5	Ni	0.6141	0.6147	0.6153	0.6160	0.6166		
	Nb	0.1764	0.1765	0.1767	0.1769	0.1771		
	Ta	0.0411	0.0823	0.1235	0.1649	0.2063		
	K	0.1685	0.1265	0.0844	0.0422	0.0000		
	M	36.4	36.5	42.3	40.1	39.0		
6	Ni	0.6222	0.6228	0.6235	0.6241	0.6247	0.6254	
	Nb	0.1228	0.1230	0.1231	0.1232	0.1233	0.1235	
	Ta	0.0416	0.0834	0.1252	0.1671	0.2091	0.2511	
	K	0.2134	0.1709	0.1283	0.0856	0.0429	0.0000	
	M	36.9	41.5	36.1	44.4	40.2	39.3	
7	Ni	0.6305	0.6311	0.6318	0.6324	0.6331	0.6338	0.6345
	Nb	0.0679	0.0680	0.0680	0.0681	0.0682	0.0683	0.0683
	Ta	0.0422	0.0845	0.1268	0.1693	0.2119	0.2545	0.2972
	K	0.2595	0.2164	0.1733	0.1301	0.0869	0.0435	0.0000
	M	39.7	40.4	38.8	51.4	45.6	42.9	43.9

Table 17. Ethane conversion of Ni-Nb-Ta-K oxide mixtures listed in Table 16

	1	2	3	4	5	6	7
	Ethane Conversion, %						
1	6.3						
2	4.9	6.0					
3	4.5	5.3	6.3				
4	4.4	4.5	5.7	7.0			
5	3.0	4.4	5.1	6.1	6.5		
6	0.8	2.7	3.8	5.1	5.4	6.5	
7	0.3	0.9	2.3	4.2	5.1	6.3	5.8

Table 18. Ethylene Selectivity of Ni-Nb-Ta-K oxide mixtures listed in Table 16 at 300°C

	1	2	3	4	5	6	7
	Ethylene Selectivity, %						
1	80.6						
2	62.3	84.8					
3	45.5	68.4	85.2				
4	34.4	49.4	73.1	84.6			
5	16.3	35.4	55.4	76.9	85.9		
6	1.3	17.4	37.2	54.6	80.9	85.2	
7	0.0	1.0	8.7	39.1	59.1	78.3	86.9

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Table 19. Composition and mass of bulk Ni-Nb-Ta oxide mixtures

		1	2	3	4	5	6	7
		Mole Fraction & Sample Mass, mg						
1	Ni	0.95						
	Nb	0.03						
	Ta	0.02						
	M	28.2						
2	Ni	0.91	0.89					
	Nb	0.03	0.09					
	Ta	0.06	0.02					
	M	43.7	51.8					
3	Ni	0.87	0.85	0.83				
	Nb	0.03	0.09	0.15				
	Ta	0.10	0.06	0.02				
	M	47.6	35.2	39.2				
4	Ni	0.82	0.80	0.78	0.77			
	Nb	0.04	0.10	0.16	0.21			
	Ta	0.14	0.10	0.06	0.02			
	M	53.1	40.5	38.8	35.8			
5	Ni	0.78	0.76	0.74	0.72	0.70		
	Nb	0.04	0.10	0.16	0.22	0.27		
	Ta	0.19	0.14	0.10	0.06	0.02		
	M	39.8	52.1	38.1	37.5	36.8		
6	Ni	0.73	0.71	0.69	0.67	0.66	0.64	
	Nb	0.04	0.10	0.17	0.23	0.28	0.34	
	Ta	0.24	0.19	0.14	0.10	0.06	0.02	
	M	70.1	42.4	37.1	40.2	37.0	39.6	
7	Ni	0.67	0.66	0.64	0.62	0.61	0.59	0.58
	Nb	0.04	0.11	0.17	0.23	0.29	0.35	0.40
	Ta	0.29	0.24	0.19	0.14	0.10	0.06	0.02
	M	35.6	45.2	36.1	42.0	35.6	36.1	38.2

Table 20. Ethane conversion of Ni-Nb-Ta oxide mixtures listed in Table 19

	1	2	3	4	5	6	7
	Ethane Conversion, %						
1	2.0						
2	4.1	3.8					
3	3.8	6.1	7.9				
4	4.1	2.6	5.3	6.1			
5	2.8	3.8	4.5	6.9	6.4		
6	5.4	3.2	6.6	3.3	7.1	6.4	
7	3.9	3.9	5.2	3.7	5.3	7.0	6.1

Table 21. Ethylene selectivity of Ni-Nb-Ta oxide mixtures listed in Table 19

	1	2	3	4	5	6	7
	Ethylene Selectivity, %						
1	70.8						
2	69.3	63.4					
3	68.5	74.3	68.4				
4	61.9	62.0	74.5	69.9			
5	59.8	67.4	69.7	74.6	76.5		
6	74.9	65.2	76.0	67.2	76.4	75.8	
7	75.5	67.3	73.0	72.1	72.2	80.0	75.3

Table 22. Composition and mass of Ni-Nb-Ta oxide mixtures

		1	2	3	4	5	6	7
		Mole Fraction & Sample Mass, mg						
1	Ni	0.8621						
	Nb	0.0690						
	Ta	0.0690						
	M	39.3						
2	Ni	0.8128	0.8128					
	Nb	0.0725	0.1147					
	Ta	0.1147	0.0725					
	M	35.4	38.5					
3	Ni	0.7583	0.7583	0.7583				
	Nb	0.0763	0.1208	0.1654				
	Ta	0.1654	0.1208	0.0763				
	M	43.7	43.2	39.7				
4	Ni	0.6977	0.6977	0.6977	0.6977			
	Nb	0.0806	0.1276	0.1747	0.2217			
	Ta	0.2217	0.1747	0.1276	0.0806			
	M	50.8	38.1	38.2	36.9			
5	Ni	0.6298	0.6298	0.6298	0.6298	0.6298		
	Nb	0.0854	0.1353	0.1851	0.2349	0.2848		
	Ta	0.2848	0.2349	0.1851	0.1353	0.0854		
	M	48.9	43.6	47.5	48.3	41.8		
6	Ni	0.5533	0.5533	0.5533	0.5533	0.5533	0.5533	
	Nb	0.0909	0.1439	0.1969	0.2499	0.3029	0.3559	
	Ta	0.3559	0.3029	0.2499	0.1969	0.1439	0.0909	
	M	28.3	48.5	46.4	47.9	40.0	56.0	
7	Ni	0.4664	0.4664	0.4664	0.4664	0.4664	0.4664	0.4664
	Nb	0.0970	0.1536	0.2102	0.2668	0.3234	0.3800	0.4366
	Ta	0.4366	0.3800	0.3234	0.2668	0.2102	0.1536	0.0970
	M	51.8	34.1	49.2	35.7	42.5	47.5	62.7

Table 23. Ethane Conversion at 300 °C of Ni-Nb-Ta oxide mixtures listed in Table 22

	1	2	3	4	5	6	7
	Ethane Conversion, %						
1	9.6						
2	10.2	10.1					
3	10.6	10.9	8.2				
4	11.1	9.9	9.1	8.2			
5	9.6	10.0	10.4	10.2	9.9		
6	4.5	7.2	7.1	7.2	7.1	8.9	
7	1.4	2.0	1.8	0.7	1.1	2.5	1.4

Table 24. Ethylene selectivity at 300 °C of Ni-Nb-Ta oxide mixtures listed in Table 22

	1	2	3	4	5	6	7
	Ethylene Selectivity, %						
1	80.4						
2	80.1	82.8					
3	84.0	84.5	84.5				
4	81.8	84.0	82.7	84.3			
5	86.8	84.6	86.3	86.9	87.0		
6	84.2	88.1	89.1	87.2	87.6	90.1	
7	82.5	84.7	86.6	79.4	86.6	87.8	80.5

Table 25. Ethane Conversion at 325 °C of Ni-Nb-Ta oxide mixtures listed in Table 22

	1	2	3	4	5	6	7
	Ethane Conversion, %						
1	14.6						
2	15.9	14.5					
3	15.2	16.0	12.6				
4	15.9	14.5	13.6	12.7			
5	14.3	15.5	15.4	15.2	14.8		
6	8.2	11.8	11.4	11.6	11.8	13.9	
7	2.5	3.9	3.4	1.4	1.9	5.0	2.7

Table 26. Ethylene selectivity at 325 °C of Ni-Nb-Ta oxide mixtures listed in Table 22

	1	2	3	4	5	6	7
	Ethylene Selectivity, %						
1	84.2						
2	81.7	84.5					
3	83.9	84.9	84.3				
4	82.5	86.0	83.4	84.6			
5	87.8	86.8	85.9	86.8	87.8		
6	83.8	87.5	88.2	87.8	86.1	88.9	
7	81.5	84.2	86.0	77.2	85.2	86.4	78.5

Table 27. Difference in ethylene concentration between reactor effluent and feed for Ni-Nb-Ta oxide mixtures listed in Table 22 (C_2H_6/C_2H_4 Feed)

	1	2	3	4	5	6	7
	Δ C_2H_4, %						
1	7.0						
2	7.2	6.2					
3	5.1	6.4	5.0				
4	6.8	6.6	4.7	5.3			
5	7.3	7.3	5.9	7.1	7.1		
6	4.0	5.6	5.4	5.7	5.3	6.1	
7	1.2	2.0	1.4	-0.4	0.8	2.2	1.0

Table 28. Difference in ethane concentration between reactor effluent and feed for Ni-Nb-Ta oxide mixtures listed in Table 22 (C_2H_6/C_2H_4 Feed)

	1	2	3	4	5	6	7
	Δ C_2H_6, %						
1	-9.3						
2	-10.5	-8.3					
3	-8.1	-9.3	-7.4				
4	-9.9	-8.6	-7.2	-7.5			
5	-8.9	-9.3	-8.4	-9.4	-8.8		
6	-5.3	-7.1	-6.8	-7.1	-7.3	-7.9	
7	-1.3	-2.3	-1.7	0.4	-0.8	-2.9	-1.3

Table 29. Difference in carbon monoxide and carbon dioxide between reactor effluent and feed for Ni-Nb-Ta oxide mixtures listed in Table 22 (C_2H_6/C_2H_4 Feed)

	1	2	3	4	5	6	7
	Δ CO & CO_2, %						
1	2.2				.		
2	3.3	2.2					
3	2.9	2.9	2.4				
4	3.1	1.9	2.5	2.2			
5	1.7	1.9	2.5	2.3	1.8		
6	1.3	1.5	1.4	1.4	1.9	1.8	
7	0.1	0.3	0.3	0.0	0.0	0.7	0.3

Table 30. Composition and mass of Ni-Nb-Ta oxide mixtures

		1	2	3	4	5	6
		Mole Fraction & Sample Mass, mg					
1	Ni	0.7194	0.7196	0.7197	0.7199	0.7201	0.7202
	Nb	0.2324	0.1937	0.1550	0.1163	0.0775	0.0388
	Ta	0.0481	0.0867	0.1252	0.1638	0.2024	0.2410
	M	44.6	42.8	38.4	37.1	48.8	41.5
2	Ni	0.6959	0.6960	0.6962	0.6964	0.6965	0.6967
	Nb	0.2519	0.2100	0.1680	0.1261	0.0841	0.0420
	Ta	0.0522	0.0940	0.1358	0.1776	0.2194	0.2613
	M	40.1	40.5	39.0	36.8	44.4	49.9
3	Ni	0.6680	0.6682	0.6683	0.6685	0.6687	0.6689
	Nb	0.2750	0.2293	0.1835	0.1376	0.0918	0.0459
	Ta	0.0570	0.1026	0.1482	0.1939	0.2395	0.2852
	M	35.6	37.0	40.7	41.0	44.2	51.9
4	Ni	0.6345	0.6346	0.6348	0.6350	0.6352	0.6354
	Nb	0.3028	0.2524	0.2020	0.1515	0.1011	0.0505
	Ta	0.0627	0.1129	0.1632	0.2135	0.2638	0.3141
	M	37.9	38.6	37.0	34.8	35.9	36.4
5	Ni	0.5934	0.5936	0.5938	0.5940	0.5942	0.5944
	Nb	0.3368	0.2808	0.2247	0.1686	0.1124	0.0562
	Ta	0.0698	0.1256	0.1815	0.2374	0.2934	0.3494
	M	36.5	36.0	36.6	41.5	35.6	35.4
6	Ni	0.5420	0.5422	0.5424	0.5426	0.5428	0.5430
	Nb	0.3794	0.3163	0.2531	0.1899	0.1267	0.0633
	Ta	0.0786	0.1414	0.2045	0.2675	0.3306	0.3937
	M	36.8	38.1	39.9	39.2	33.9	35.8

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Table 31. Ethane Conversion at 300 °C of Ni-Nb-Ta oxide mixtures listed in Table 30

	1	2	3	4	5	6
	Ethane Conversion, %					
1	5.8	3.8	3.3	4.3	5.2	4.1
2	3.8	4.4	4.5	3.8	3.9	3.7
3	7.5	9.6	10.3	7.6	6.1	6.9
4	7.8	7.5	8.4	9.1	9.8	9.9
5	8.5	8.1	8.2	8.9	9.2	10.2
6	9.6	9.1	10.3	10.4	10.7	11.6

Table 32. Ethylene selectivity at 300 °C of Ni-Nb-Ta oxide mixtures listed in Table 30

	1	2	3	4	5	6
	Ethylene Selectivity, %					
1	87.2	88.0	88.2	89.4	89.3	89.6
2	86.4	87.1	89.2	90.4	87.3	87.7
3	85.1	84.4	81.8	85.4	90.5	89.0
4	82.8	84.0	85.2	85.4	83.5	83.8
5	80.2	83.1	84.6	85.0	85.5	85.9
6	77.5	78.1	81.5	84.1	83.3	85.3

Table 33. Ethane conversion at 325 °C of Ni-Nb-Ta oxide mixtures listed in Table 30

	1	2	3	4	5	6
	Ethane Conversion, %					
1	8.7	6.7	5.7	7.3	8.8	6.8
2	6.7	7.3	7.2	6.2	6.5	6.3
3	11.7	13.3	13.9	11.5	9.6	11.1
4	12.2	11.7	12.2	12.8	14.0	14.4
5	12.8	12.0	13.0	13.7	14.0	15.4
6	14.1	14.0	15.9	15.6	16.5	16.9

Table 34. Ethylene selectivity at 325 °C of Ni-Nb-Ta oxide mixtures listed in Table 30

	1	2	3	4	5	6
	Ethylene Selectivity					
1	85.7	85.6	85.9	86.8	87.5	88.6
2	84.4	85.1	86.3	88.1	85.6	85.6
3	84.3	83.7	84.9	84.8	89.4	88.0
4	84.0	83.8	85.4	84.0	85.2	84.5
5	81.3	83.9	84.1	84.5	84.5	85.9
6	82.3	81.4	83.5	84.2	85.0	85.8

Table 35. Difference in ethylene concentration between reactor effluent and feed for Ni-Nb-Ta oxide mixtures listed in Table 30 (C_2H_6/C_2H_4 Feed)

	1	2	3	4	5	6
	$\Delta\ C_2H_4$, %					
1	2.3	1.1	0.6	0.4	. 2.3	1.8
2	1.2	1.2	0.5	1.2	1.5	0.9
3	3.1	4.6	5.6	4.2	3.7	4.2
4	4.6	4.1	4.4	4.2	5.5	5.4
5	3.7	4.2	4.6	4.6	4.0	6.1
6	6.0	5.3	5.9	5.0	6.8	7.0

Table 36. Difference in ethane concentration between reactor effluent and feed for Ni-Nb-Ta oxide mixtures listed in Table 30 (C_2H_6/C_2H_4 Feed)

	1	2	3	4	5	6
	$\Delta\ C_2H_6$, %					
1	-3.8	-2.8	-2.1	-2.4	-4.2	-3.1
2	-2.9	-3.0	-2.3	-2.7	-2.9	-2.5
3	-5.6	-7.0	-8.3	-6.2	-5.1	-5.9
4	-6.6	-6.2	-6.8	-6.6	-7.7	-7.8
5	-6.5	-6.5	-6.8	-7.0	-6.8	-9.0
6	-8.3	-8.0	-8.7	-8.1	-9.8	-9.9

Table 37. Difference in carbon monoxide and carbon dioxide between reactor effluent and feed for Ni-Nb-Ta oxide mixtures listed in Table 30 (C_2H_6/C_2H_4 Feed)

	1	2	3	4	5	6
	$\Delta\ CO\ \&\ CO_2$, %					
1	1.5	1.7	1.5	1.9	1.9	1.4
2	1.7	1.8	1.8	1.4	1.4	1.6
3	2.5	2.5	2.6	2.1	1.4	1.7
4	1.9	2.1	2.4	2.4	2.2	2.5
5	2.8	2.3	2.3	2.4	2.8	2.9
6	2.3	2.6	2.9	3.1	3.0	2.9

Table 38. Composition and mass of Ni-Nb-Ta oxide mixtures calcined at 300°C

		1	2	3	4	5	6
		Mole Fraction & Sample Mass, mg					
1	Ni	1.000					
	Nb	0.000					
	Ta	0.000					
	M	56.1					
2	Ni	0.883	0.890				
	Nb	0.000	0.110				
	Ta	0.117	0.000				
	M	46.0	58.0				
3	Ni	0.782	0.787	0.793			
	Nb	0.000	0.103	0.208			
	Ta	0.218	0.110	0.000			
	M	45.4	57.2	47.7			
4	Ni	0.693	0.698	0.702	0.706		
	Nb	0.000	0.097	0.195	0.294		
	Ta	0.307	0.206	0.104	0.000		
	M	49.9	46.5	45.2	50.0		
5	Ni	0.615	0.618	0.622	0.626	0.629	
	Nb	0.000	0.091	0.183	0.276	0.371	
	Ta	0.385	0.291	0.195	0.098	0.000	
	M	51.5	52.0	47.5	55.3	54.2	
6	Ni	0.545	0.548	0.551	0.554	0.557	0.560
	Nb	0.000	0.086	0.173	0.261	0.350	0.440
	Ta	0.455	0.366	0.276	0.185	0.093	0.000
	M	54.5	54.6	57.2	59.6	54.3	50.8

Table 39. Ethane Conversion at 300 °C of Ni-Nb-Ta oxide mixtures listed in Table 38

	1	2	3	4	5	6
	Ethane Conversion, %					
1	10.5					
2	12.0	17.7				
3	18.9	19.2	15.4	·		
4	18.6	18.4	20.0	--		
5	18.6	19.9	20.0	20.5	19.0	
6	15.2	18.9	16.9	19.0	18.1	16.9

Table 40. Ethylene selectivity at 300 °C of Ni-Nb-Ta oxide mixtures listed in Table 38

	1	2	3	4	5	6
	Ethylene Selectivity, %					
1	53.6					
2	54.9	81.6				
3	83.3	83.9	77.4			
4	83.3	84.4	85.2	--		
5	84.4	85.1	86.1	86.2	84.7	
6	83.9	84.6	84.2	86.0	84.8	80.9

Table 41. Ethane Conversion at 250 °C of Ni-Nb-Ta oxide mixtures listed in Table 38

	1	2	3	4	5	6
	Ethane Conversion, %					
1	5.4					
2	5.7	9.7				
3	9.8	11.0	5.9			
4	9.8	4.5	5.5	--		
5	4.6	4.5	4.6	5.1	4.5	
6	2.9	4.1	3.3	4.5	4.2	4.0

Table 42. Ethylene selectivity at 250 °C of Ni-Nb-Ta oxide mixtures listed in Table 38

	1	2	3	4	5	6
	Ethylene Selectivity, %					
1	27.6					
2	32.8	76.2				
3	79.9	79.9	68.6			
4	78.6	77.4	81.6	--		
5	77.5	80.4	84.4	85.0	76.4	
6	81.7	79.3	81.1	85.5	78.3	69.9

Table 43. Difference in ethylene concentration between reactor effluent and feed for Ni-Nb-Ta oxide mixtures listed in Table 38 (C_2H_6/C_2H_4 Feed)

	1	2	3	4	5	6
	ΔC_2H_4, %					
1						
2						
3						
4		7.3	6.3			
5	6.5	7.4	6.1	6.4	7.2	
6	5.4	7.1	5.2	6.0	7.0	5.6

Table 44. Difference in ethane concentration between reactor effluent and feed for Ni-Nb-Ta oxide mixtures listed in Table 38 (C_2H_6/C_2H_4 Feed)

	1	2	3	4	5	6
	ΔC_2H_6, %					
1						
2						
3						
4		-10.3	-9.8			
5	-9.7	-10.8	-9.3	-9.7	-10.3	
6	-7.9	-10.2	-8.2	-9.2	-10.0	-8.9

Table 45. Difference in carbon monoxide and carbon dioxide between reactor effluent and feed for Ni-Nb-Ta oxide mixtures listed in Table 38 (C_2H_6/C_2H_4 Feed)

	1	2	3	4	5	6
	Δ CO & CO_2, %					
1						
2						
3						
4		3.0	3.6			
5	3.2	3.5	3.2	3.4	3.2	
6	2.5	3.2	3.0	3.2	3.1	3.4

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Table 46. Composition and mass of Ni-Nb, Ni-Co, Ni-Co-Nb, Ni-Nb-Al, Ni-Nb-Fe, and Mo-V-Nb oxide mixtures; difference in ethane and ethylene concentration between reactor effluent and feed; carbon monoxide and carbon dioxide production.

Sample ID	ΔC_2H_4 %	ΔC_2H_6 %	ΔCO & CO_2, %	m, mg	Mole Fraction				
					Ni	Co	Nb	Al	Fe
MoVNb	-1.1	-0.4	1.8	40.8					
Blank	0.2	-0.3	0.4	0.0					
21187.12	3.4	-6.0	3.0	39.4	0.60	0.00	0.36	0.05	0.00
21187.31	4.0	-7.2	3.5	41.5	0.61	0.00	0.36	0.00	0.02
21187.32	3.3	-6.8	3.8	38.9	0.60	0.00	0.36	0.00	0.05
21187.33	2.0	-5.6	3.9	40.7	0.58	0.00	0.35	0.00	0.07
10717.31	4.7	-6.8	2.4	41.2	0.85	0.00	0.15	0.00	0.00
10717.41	6.7	-9.9	3.5	39.9	0.77	0.00	0.23	0.00	0.00
10717.42	7.2	-10.3	3.4	40.2	0.81	0.04	0.16	0.00	0.00
10717.52	7.3	-10.5	3.5	41.8	0.73	0.04	0.23	0.00	0.00
10717.53	2.3	-5.1	3.0	40.6	0.76	0.08	0.16	0.00	0.00
10717.62	0.7	-5.6	5.2	40.1	0.65	0.04	0.31	0.00	0.00
10717.63	4.7	-8.2	3.8	41.6	0.68	0.08	0.24	0.00	0.00
10717.71	5.7	-8.4	3.0	41.0	0.55	0.00	0.45	0.00	0.00
MoVNb	0.00	-1.4	1.8	40.9					
10717.72	6.5	-10.5	4.3	40.5	0.58	0.04	0.39	0.00	0.00
10717.73	-5.1	0.6	4.8	41.3	0.60	0.08	0.32	0.00	0.00
10615.41	2.7	-6.1	3.8	40.3	0.70	0.00	0.30	0.00	0.00
10615.42	3.2	-6.7	3.8	40.8	0.70	0.10	0.20	0.00	0.00
10615.51	1.6	-3.8	2.5	39.5	0.60	0.00	0.40	0.00	0.00
10615.52	1.6	-5.7	4.3	38.3	0.60	0.10	0.30	0.00	0.00
21122.21	4.6	-8.6	4.3	39.4	0.84	0.01	0.15	0.00	0.00
21122.22	2.3	-6.6	4.6	32.2	0.81	0.01	0.18	0.00	0.00
21122.23	4.0	-7.7	4.0	39.6	0.78	0.01	0.21	0.00	0.00
Blank	-0.3	0.2	0.4	0.0					
21122.24	4.8	-9.4	4.9	40.3	0.75	0.01	0.24	0.00	0.00
21122.25	3.5	-7.4	4.2	40.1	0.73	0.01	0.26	0.00	0.00
21122.13	4.7	-9.2	4.7	39.9	0.79	0.00	0.21	0.00	0.00
21122.14	4.5	-8.4	4.2	38.8	0.76	0.00	0.24	0.00	0.00
21122.31	4.6	-8.2	3.9	38.9	0.83	0.02	0.15	0.00	0.00
21122.33	5.6	-9.1	3.8	39.3	0.77	0.02	0.21	0.00	0.00
21122.42	4.8	-8.4	3.9	39.1	0.79	0.03	0.18	0.00	0.00
21122.43	5.6	-10.4	5.1	42.2	0.77	0.03	0.21	0.00	0.00
21123.1	6.2	-10.6	4.7	40.6	0.69	0.00	0.31	0.00	0.00
21123.2	5.6	-9.9	4.6	40.3	0.67	0.00	0.33	0.00	0.00
21123.3	5.6	-9.1	3.8	42.0	0.65	0.00	0.35	0.00	0.00
21123.5	5.2	-8.1	3.1	40.3	0.61	0.00	0.39	0.00	0.00
21123.7	5.6	-8.2	2.9	40.3	0.59	0.00	0.41	0.00	0.00

Sample ID	Δ C₂H₄ %	Δ C₂H₆ %	Δ CO & CO₂, %	m, mg	Mole Fraction				
					Ni	Co	Nb	Al	Fe
MoVNb	2.1	-3.4	1.6	41.9					
10652.31	8.7	-12.6	4.2	41.7	0.80	0.00	0.20	0.00	0.00
10652.41	6.4	-10.6	4.5	38.5	0.70	0.00	0.30	0.00	0.00
10652.61	3.7	-5.9	2.5	39.7	0.50	0.00	0.50	0.00	0.00
10793.1	8.3	-10.5	2.5	39.2	0.86	0.00	0.14	0.00	0.00
10793.3	8.1	-10.4	2.6	39.1	0.81	0.00	0.19	0.00	0.00
10793.5	5.5	-6.9	1.7	37.9	0.75	0.00	0.25	0.00	0.00

Table 47. Composition of Ni-Nb oxide mixtures

		1	2	3	4
		Mole Fraction & Sample Mass, mg			
1	Ni	0.8772	0.7692	0.6736	0.5882
	Nb	0.1228	0.2308	0.3264	0.4118
	M	17.1	36.9	39.3	36.5
2	Ni	0.8772	0.7692	0.6736	0.5882
	Nb	0.1228	0.2308	0.3264	0.4118
	M	37.4	37.2	40.3	39.0
3	Ni	0.8772	0.7692	0.6736	0.5882
	Nb	0.1228	0.2308	0.3264	0.4118
	M	42.1	42.4	48.3	41.0
4	Ni	0.8772	0.7692	0.6736	0.5882
	Nb	0.1228	0.2308	0.3264	0.4118
	M	50.3	39.3	38.0	39.7
5	Ni	0.8772	0.7692	0.6736	0.5882
	Nb	0.1228	0.2308	0.3264	0.4118
	M	37.8	39.1	48.9	50.4
6	Ni	0.8772	0.7692	0.6736	0.5882
	Nb	0.1228	0.2308	0.3264	0.4118
	M	36.6	38.3	39.0	40.4

Table 48. Ethane Conversion of Ni-Nb oxide mixtures listed in Table 47

	Precipitation Method	1	2	3	4
		Ethane Conversion, %			
1	NH₄OH	0.9	8.9	7.3	6.8
2	NEt₄OH	8.9	6.2	8.6	11.4
3	K₂CO₃	0.0	0.0	0.0	0.1
4	NaOH	0.3	2.4	3.6	4.2
5	KOH	0.5	0.2	0.0	0.1
6	(NH₄)₂CO₃	10.7	11.2	11.4	10.5

Table 49. Ethylene Selectivity of Ni-Nb oxide mixtures listed in Table 47

	Precipitation Method	1	2	3	4
		Ethylene Selectivity, %			
1	NH$_4$OH	78.3	78.8	74.5	72.3
2	NEt$_4$OH	82.4	88.0	88.1	83.1
3	K$_2$CO$_3$	0.0	50.1	27.3	0.0
4	NaOH	3.4	15.0	21.8	21.8
5	KOH	3.5	4.5	0.0	0.0
6	(NH$_4$)$_2$CO$_3$	80.7	82.6	87.1	83.6

Table 50. Composition and mass of Ni-Ta oxide mixtures; ethane conversion and ethylene
selectivity

	Mole Fraction & Sample Mass, mg	Ethane Conversion %	Ethylene Selectivity %
Ni	0.50	8.1	87.8
Ta	0.50		
m	81.8		
Ni	0.55	8.0	89.5
Ta	0.45		
m	59.2		
Ni	0.61	8.6	86.6
Ta	0.39		
m	55.8		
Ni	0.67	7.9	85.8
Ta	0.33		
m	41.5		
Ni	0.74	8.8	86.9
Ta	0.26		
m	41.4		
Ni	0.81	9.5	87.4
Ta	0.19		
m	43.3		

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